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ORGANIC CHEMISTRY

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To Our Parents and to Cathy

Organic Chemistry

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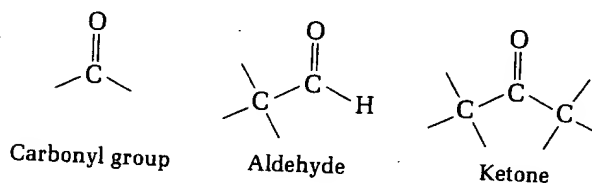
CHAPTER 9

Aldehydes and Ketones; Addition Reactions of the Carbonyl Group

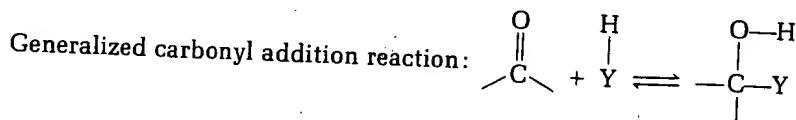
General Properties

9.1 Introduction

In Chapter 8 we made use of aldehydes and ketones as synthetic intermediates. It is time to discuss the properties of these important substances. As we have noted, aldehydes and ketones are the simplest examples of substances containing the carbonyl functional group:



This group and the alkene function vie for the title of the most versatile in organic chemistry, and in fact, the chemistry of carbonyl functions is the major topic in six later chapters in this text. Here, we concentrate on carbonyl addition reactions. We have already considered Grignard addition, which is one example of this reaction class. Others provide useful synthetic intermediates, and many appear in the chemical transformations of living systems.



9.2 Nomenclature

The IUPAC names of aldehydes are derived from the names of the corresponding alkane. The longest chain containing the $-\text{CHO}$ group is the parent structure, and the name of the corresponding alkane is changed by replacing its final $-e$ by $-al$. For example, the hydrocarbon butane becomes butanal, the aldehyde. Any chemical name that ends in $-al$ represents an aldehyde.

The Organic Chemistry of Sulfur and Phosphorus

34-13 Comparisons between Oxygen and Sulfur

Sulfur lies below oxygen in the same column of the periodic table and therefore has the same complement of six electrons in its valence shell. The top half of Table 34-3 shows obvious analogies between the two sets of functional groups. In many respects, thiols behave like alcohols, thioethers like ethers, and sulfonium ions like oxonium ions. A closer inspection reveals many important differences. Thiols are considerably stronger acids than alcohols, yet their conjugate bases are much stronger nucleophiles. Unlike alkoxides, thiolate anions form very strong complexes with many transition metals and with heavy-metal cations, e.g., lead, copper, silver, and mercury. (The older name for thiol is mercaptan, a term coined to refer to the affinity for mercury.)

Table 34-3 Sulfur-Containing Functional Groups

Parallels between functional groups containing O and S				
ROH	ROR	$\text{RO}^+\begin{matrix} \text{R} \\ \text{R} \end{matrix}$	$\text{R}-\text{C}(=\text{O})-\text{R}$	
Alcohol	Ether	Oxonium ion	Carbonyl	
RSH	RSR	$\text{RS}^+\begin{matrix} \text{R} \\ \text{R} \end{matrix}$	$\text{R}-\text{C}(=\text{S})-\text{R}$	
Thiol (mercaptan)	Thioether	Sulfonium ion	Thiocarbonyl	
Oxidized functional groups of S				
RSSR	$\text{R}-\text{S}(=\text{O})-\text{R}$	$\text{R}-\text{S}(=\text{O})_2-\text{R}$	$\text{R}-\text{S}(=\text{O})-\text{OH}$	$\text{R}-\text{S}(=\text{O})_2-\text{OH}$
Disulfide	Sulfoxide	Sulfone	Sulfinic acid	Sulfonic acid

A more important difference is the ready oxidation of thiols and thioethers to a series of new functional groups, shown in the bottom half of Table 34-3. The disulfide is the sulfur analog of a peroxide but is much more stable. The other groups have no stable analogs in oxygen chemistry.

A final difference between sulfur and oxygen is the instability of the thiocarbonyl function. With certain exceptions (CS_2 is the major example), the $\text{R}_2\text{C}=\text{S}$ group is very labile to addition reactions. Alkyl thioaldehydes and ketones can be generated only as fleeting intermediates that rapidly dimerize or trimerize. The chemistry of thiocarbonyl derivatives is a comparatively insignificant chapter of organosulfur chemistry.

These behavioral differences can be explained in part by considering bonding properties of the elements. Sulfur is a larger, less electronegative, and more polarizable element than oxygen, and its anions form relatively weak hydrogen bonds. These properties play determining roles in the high nucleophilicity of sulfur. Relative to their oxygen counterparts, single C—S and H—S bonds are weak and —S—S— bonds are stronger (Section 29-5).